October 22, 2004

RRD OPERATIONAL MEMORANDUM NO. 2

SUBJECT: SAMPLING AND ANALYSIS – ATTACHMENT 6
SAMPLING METHODS FOR VOLATILE ORGANIC COMPOUNDS

Key definitions for terms used in this document:

NREPA:	The Natural Resources and Environmental Protection Act, 1994 PA 451, as amended
Part 201:	Part 201, Environmental Remediation, of NREPA
Part 211:	Part 211, Underground Storage Tank Regulations, of NREPA
Part 213:	Part 213, Leaking Underground Storage Tanks, of NREPA
MDEQ:	Michigan Department of Environmental Quality
RRD:	Remediation and Redevelopment Division
U.S. EPA:	United States Environmental Protection Agency
Contact time:	The time from when the sample was preserved with methanol to the time the aliquot was taken for analysis, or the time the sample was in contact with the methanol prior to analysis.
Criteria or criterion:	Includes the cleanup criteria for Part 201 and the Risk-based Screening Levels as defined in Part 213 and R 299.5706a(4)
Facility:	Includes "facility" as defined by Part 201 and "site" as defined by Part 213
Method 5035A:	U.S.EPA Method 5035, "Closed-System Purge-and-Trap and Extraction for Volatiles Organics in Soil and Waste Samples," Test Method for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, USEPA, Office of Solid Waste and Emergency Response, Dec 1996, Third Edition.
Method 5021A:	U.S.EPA Method 5021A, "Volatile Organic Compounds in Various Sample Matrices Using Equilibrium Headspace Analysis", Test Method for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, U.S.EPA, Office of Solid Waste and Emergency Response, Dec 1996, Third Edition.
Response Actions:	Includes "response activities" as defined by Part 201 and "corrective action" as defined by Part 213
Sonication:	The procedure for mixing the soil with methanol using sound waves.

PURPOSE

This attachment to RRD Operational Memorandum No. 2 provides direction for the collection and preservation of soil samples using the procedures in U.S.EPA Methods 5035A and 5021A for analysis to determine concentrations volatile organic compounds (VOCs). This attachment is applicable for site assessments, site investigations, and response activities under Part 201, Part 211, and Part 213.

To produce reliable representative analytical results, the MDEQ implemented the use of the methanol preservation procedures for the preservation of soil samples collected for analysis to determine concentrations of VOCs on April 30, 1998.

INTRODUCTION

The requirements for collection and preservation of samples are based on the latest revisions of U.S. EPA Methods 5035A and 5021A. The applicable contaminants that can be measured are listed within the methods. Other contaminants may be included if method performance data exists for the contaminant that demonstrates the accuracy, precision and detection that can be measured.

Guidance on applicable target detection limits (TDLs) and available analytical methods are included in RRD Operational Memorandum No. 2, Attachment 1.

USE OF PROCEDURES WITHIN METHODS 5035A and 5021A

Method 5035A includes several procedures for the collection and preparation of soils for VOCs analysis. These include high concentration methods (methanol preservation), sealed samplers using soil coring devices, and the low concentration soil method using sealed containers for direct attachment to the analytical instrument. Method 5021A provides for the sample preparation of both waters and soils using sealed containers.

Method 5035A, High Concentration Method – Option 1, Methanol Preservation

The MDEQ accepts results generated using the high concentration soil method of Method 5035A for site assessment, site investigations, and response activities, provided the requirements listed below are followed and documented:

- Samples are preserved with methanol in the field using a procedure consistent with that provided in this document.
- At least ten grams of soil are collected.
- The ratio of methanol volume to soil weight is equal to or greater than one.
- Samples are sonicated for at least 20 minutes as soon as possible upon receipt at the lab.
- An aliquot of methanol is taken immediately after sonication, and stored for analysis.
- The sample with methanol is not used for analysis of volatiles once the aliquot of methanol is taken.
- The laboratory standard operating procedures provide the information listed within this document's section entitled Laboratory Related Procedures and Documentation.
- Operational Memorandum No. 2, Attachment 1, Target Detection Limits and Available Methods direction has been followed.

Method 5035A, High Concentration Method – Option 2, Bulk Sampling

The bulk sampling procedure in Method 5035A does not produce a reliable representative sample because it is susceptible to volatilization and biodegradation. Therefore, the MDEQ does not accept results generated using bulk sampling procedures, unless acceptable justification is provided that documents the nature of the sample prevents sampling by the procedures described as acceptable in this document.

Method 5035A, Low Concentration Method

The MDEQ accepts results generated using the low concentration soil method of Method 5035A, for site assessment, site investigations, and response activities, provided the requirements listed below are followed and documented:

- The sealed containers are attached directly to the instrumentation.

- The preservation is applied correctly to the various soil types.
- Information that validates the use of the method with the appropriate type of soil is provided.
- Information that demonstrates the effectiveness of the sealed containers ability to prevent the exposure of the sample to environmental conditions is provided.

The low concentration preservation procedure may not be appropriate for all soil types. For example, calcareous soils cannot be sampled by the low concentration method when sodium bisulfate is used because a chemical reaction occurs that adversely affects the results. Soil samples must be tested in the field prior to collecting the samples for analyses, as discussed in Method 5035A, to determine if the acidic preservation for the low concentration procedure can be used. If the acidic preservation cannot be used, alternate procedures for preservation in Method 5035A should be used. The preferable alternate procedure is to extrude the samples into empty sealed vials and freeze on site to < -7 Cº. Care must be taken to not freeze the vials below -20 Cº to avoid potential problems with vial seals.

Method 5021A, Headspace Analysis using Sealed Containers

The MDEQ accepts results generated using the sample collection and preservation methods of Method 5021A for site assessment, site investigations, and response activities, provided the same requirements for Method 5035A, Low Concentration Method are documented. The preferred analytical method is Method 8260B (see RRD Operational Memorandum No. 2, Attachment 1). This sample and collection procedure is highly recommended for the analyses of contaminants that are very soluble in water.

Method 5035A, Soil Coring Devices (used to transfer samples to the laboratory)

The MDEQ requires the use of soil coring devices to evaluate the leaching of volatiles from soils, as provided in Operational Memorandum No. 2, Attachment 2, Soil Leaching Methods. The requirements in Attachment 2 must be met.

The MDEQ does not recommend the use of soil coring devices for initial site characterization where the objectives include establishing the contaminants of concern; or for response activities where the objectives are to demonstrate final compliance with cleanup criteria. The MDEQ may accept results using the soil coring devices, providing the following requirements are documented:

- Scientific studies exist that demonstrate the device to be effective for the use intended. The manufacturer of the device should be contacted regarding studies that prove them effective.
- The party proposing the use of the soil coring devices must demonstrate the effectiveness of the devices to retain volatile chemicals, for the specific chemicals of concern at the facility. Demonstration of the effectiveness of the devices proposed to be used can be accomplished using duplicate sampling. The demonstration must include duplicate samples collected using methanol preservation in the field. Duplicate samples must be collected for a minimum of one sample, or for at least one of every five samples collected.
- Written protocols must be established regarding the use of the devices to collect samples, and to preserve samples at the laboratory. These protocols must be provided to the MDEQ.
- Confirmation samples must be collected using methanol preservation in the field, equivalent to the standard operating procedure of this document. Confirmation samples must be collected for a minimum of two samples, or for at least two from every ten samples collected.
- All requirements of Method 5035A regarding the use of the samplers must have been met.

OXYGENATES

Oxygenates refer to methyl(tert)butylether (MTBE), t-Butyl alcohol (TBA), Di-isopropyl ether (DIPE), Ethyl(tert)butylether (ETBE), Ethyl alcohol, Methyl alcohol, and Tertiaryamylmethylether (TAME), and the oxygenated ethers refer to MTBE, DIPE, ETBE and TAME. When any of the oxygenated ethers are required for analysis, and high temperature purging is used in the analysis, samples collected must have the pH adjusted to > 10 in the field using Trisodium phosphate dodecahydrate (TSP), or two samples can be collected and the laboratory instructed to neutralize one prior to the analysis for oxygenated ethers. The laboratory should be contacted regarding its procedure for the analysis of oxygenated ethers to determine if high temperature purging is used. Methods 5035A and 5021A can be used for sampling for oxygenates, provided the requirements in this document are met. Method 5021A is highly recommended.

Questions concerning this document should be directed to Mr. A. Ralph Curtis, Toxicology Unit, RRD, at 517-373-8389, or email to mailto:mcurtisar@michigan.gov.

The following documents are rescinded with the issuance of this attachment:

- Environmental Response Division procedure for the Collection and Methanol Preservation of Soils for Volatile Organics, dated May 1, 2000.
- Storage Tank Division procedure for the Collection and Preservation of Soil Samples for Volatile Organic Analysis, dated May 18, 2000.
- Storage Tank Division Informational Memo No. 13 “Implementation of Environmental Protection Agency (EPA) SW-846 Method 5035 Closed-System Purge and Trap and Extraction for Volatile Organics in Soils and Waste Samples”, dated September 4, 1998.

APPENDAGE:

Standard Operating Procedure for Methanol Preservation in the Field

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This memorandum and its attachments are intended to provide direction and guidance to foster consistent application of Part 201, Part 211, and Part 213 and the associated administrative rules. This document is not intended to convey any rights to any parties or create any duties or responsibilities under the law. This document and matters addressed herein are subject to revision.

STANDARD OPERATING PROCEDURE for METHANOL PRESERVATION IN THE FIELD

SUMMARY

Soil samples are collected using conventional procedures, including auger and split spoon techniques. Sub-samples are then taken using syringe-type coring devices and immediately transferred into pre-weighed VOC vials containing reagent grade methanol sufficient to obtain an estimated ratio of 1:1 with the soil. The samples are transferred to the laboratory. Upon receipt at the laboratory, the following steps are taken as soon as is practical:

An accurate sample weight is determined.
The sample container is swirled gently to break up soil clumps.
The sample is sonicated for 20 minutes.
An aliquot taken and stored for analyses using Method 8260B.

Method 5035A uses a 2:1 ratio of methanol volume to soil weight. This ratio is acceptable contingent that the requirements in Operational Memorandum No. 2, Attachment 1, Target Detection Limits and Available Methods, are met.

LABORATORY RELATED PROCEDURES AND DOCUMENTATION

Procedures - The laboratory selected should have written standard operating procedures that address the provision of sampling supplies intended for methanol preservation of samples, sample receipt checks, sample preparation steps and documentation, sample collection requirements, and analyses. The laboratory should first be contacted regarding specific requirements. The laboratory's standard operating procedure governing the sample preparation should specify the contact time routinely applied, and when this time period is not met, this must be narrated with the results. The following documentation must be included:

- Copies of the certifications of the methanol used.
- Percent moisture in the samples (determined using separate vial/container with just soil).
- Dates samples were collected, and preserved if not immediately performed upon collection.
- Dates samples were received at the laboratory.
- Sample weights.
- Sample moisture (soils and sediments).
- Actual ratios of methanol to soil.
- Sonication dates/times.
- Minutes of sonications if different from 20 minutes.
- Dates/times aliquots were taken for analysis, if not taken immediately after sonification.
- The dates of the analysis.

MDEQ LABORATORY SPECIFICATIONS FOR SAMPLE COLLECTION

The following specifications apply for sample collection kit provided by the MDEQ laboratory. Other laboratories may have similar kits with specifications. Contact the laboratory selected.

Target Soil Weight = 10 grams
Allowed Weight = 9 to11 grams
Size of VOC Sampling Vials = 40 ml
Methanol Volume (provided in tubes) = 10 ml
Soil Coring Device (Syringe Sampler) Size = 10 ml
Green Sticker to Warn of Hazardous Waste
Wide Mouth Jars (4 oz. and 8 oz.)

HEALTH AND SAFETY

Material Safety and Data Sheets (MSDSs) providing health and safety data, and emergency procedures should accompany staff in the field. Methanol ampoules, tubes, and vials must be provided to field staff inside protective containers to hold any spillage. Methanol is a toxic and flammable liquid. Handle with proper safety precautions. Wear safety glasses and protective gloves. Nitrile Rubber or Viton gloves are recommended. Avoid inhalation. Store and handle in a ventilated area, away from sources of ignition and extreme heat. Store methanol in a cool place, preferably in sample coolers on ice. This is especially important for methanol in tubes, where pressure buildup due to extreme heat may result in rupture. Vials should be opened and closed quickly during collection. In the event of eye contact, immediately flush with large amounts of water for at least 15 minutes, occasionally lifting upper and lower lids. Seek medical attention immediately.

SHIPPING

The shipping of methanol is regulated by the U.S. Department of Transportation (DOT), Title 49 of the Code of Federal Regulations. The DOT number is UN 1230. The amount of methanol used for sample preservation falls under the exemption for small quantities. Requirements for shipment of samples by common carrier are as follows:

Maximum volume of methanol in a sample container cannot exceed 30 ml.
The sample container cannot be full of methanol.
Sufficient absorbent material must be used in the container to completely absorb sample content.
Each cooler must have less than 500 ml of methanol.
The cooler or package weight must not exceed 64 pounds.
Each cooler must be identified as containing less than 500 ml methanol.

APPARATUS AND MATERIALS NEEDED FOR SAMPLE COLLECTION

Absorbent Material – If the samples are to be shipped by common carrier, vermiculite or similar material, sufficient to completely absorb the methanol for each sample.

Calibration Weight - Near or equal to the target sample weight.

Certified Methanol – Methanol certified for purge and trap gas chromatography is analytically verified prior to sampling (by lot). In this procedure the methanol is provided in sealed ampoules. Some labs may provide methanol in the sampling vial.

Field Balance - Capable of holding sampling vial and syringe on the wide mouth jar used to prevent balance contamination, and measurement within + 0.2 grams.

Hazardous Waste Warning Label - Suitable vial labels to warn personnel of the presence of methanol as a preservative.

Methanol Sampling Kit/Method 5035A Sampling Kit:

Protective Wear - Nitrile rubber or Viton gloves. Splash proof safety goggles.

Plastic Bags - Air tight seals, capable of holding three sample VOC vials, and sub-coring device.

Protocol to be used for the collection of samples.

Sub-Coring Device - A syringe type device, whose material has been tested and found free of contaminants,. This device is used to sub-sample the targeted amount of soil, for transfer into methanol in the field.

Wide Mouth Jar (for holding methanol tubes) - Of suitable size to allow temporary storage and shipment of the methanol tubes.

Wide Mouth Jar (for preventing balance contamination) - Of suitable size to allow temporary storage of the syringe type sampler and VOC sample vial on the field balance.

Volatile Organic Compound (VOC) Syringe Labels - Methanol resistant labels.

VOC Vials - Vials with Teflon™ lined septa, pre-weighed, with methanol resistant labels.

SAMPLE CONTAINERS, PRESERVATION AND HOLDING TIMES

Containers - Sample containers are VOC Vials with Teflon™ lined septa of suitable size to hold the soil plus methanol, supplied with methanol resistant labels.

Preservation – Samples are preserved in the field approximately one to one ratio of soil weight to methanol volume, using pre-weighed vials and a field balance. The exact sample weights and ratios are determined at the laboratory. More methanol is added to make the ratio one to one when possible. When weights are less than the specified minimum, the reporting limit is increased. The maximum and minimum limits for the weights of soils specified by the MDEQ laboratory are provided in the section of this document entitled “Specifications for the Collection of Samples Using Methanol Preservation.”

Holding Times - The maximum allowable holding time is 14 days from sample collection to analysis. If the maximum allowable holding time is exceeded, interpret the results as minimum concentrations of the measured compounds.

QUALITY CONTROL

Field Blanks

Use - Field blanks are used to determine sample contamination that may occur during the storage, transportation, sampling, and analysis of samples. A field blank is a sample vial containing a pre-measured quantity of VOC-free methanol, obtained from the laboratory or prepared in a contaminant free environment.

Frequency - The number of field blanks depends upon project objectives and the field activities being performed at specific locations. It is recommended that a field blank be created at each location where activities may result in significant VOCs released into the environment, or for every 20 samples, whichever is more.

Interpretation – Positive results may indicate contamination from the methanol, the sample container, from the air at the site, from diffusion of air containing volatiles into the blank during transport to the laboratory, or from the laboratory environment. Compare field blank results with trip blank results and laboratory method blanks to isolate the cause. Sample results that approach the field blank results may be unusable.

Trip Blanks

Use - Methanol trip blanks are used to determine if contamination is occurring from the methanol, storage, transportation, or the field.

Frequency - One trip blank should be used per cooler.

Interpretation – Positive trip blanks can be attributed to the methanol, sample vial material, and the environment in the cooler or sample transport container. Trip blanks should be prepared at, and provided by, the laboratory in order to make this interpretation. If consistent positive results are obtained, contact the laboratory and have a trip blank prepared at the laboratory and immediately analyzed to attempt isolation of the cause.

Methanol

Only purge and trap grade methanol verified to be suitable for methanol preservation should be used. Field staff should maintain documentation of the methanol lot numbers for all associated samples. If consistently high levels of compounds are measured in methanol field blanks associated with a specific lot number, request the laboratory to verify the quality of the methanol lot used to preserve the samples.

Contamination

Contamination by airborne VOCs in the air is possible by diffusion through the vial septum during shipment, storage, collection, and analysis. To control such contamination:

Use appropriate VOC sample vials.
Avoid sources that generate VOCs such as petroleum products, especially auto exhaust fumes.
Keep sample containers in coolers as much as possible.
Collect samples quickly.
Use methanol provided in sealed ampoules, tubes, or VOC vials.

Attempt to isolate the source of contamination and incorporate appropriate procedures to avoid similar circumstances.

FIELD BALANCE CALIBRATION CHECK

The field balance calibration should be checked prior to each sampling event, and whenever necessary because of handling in the field. Record this check in the field notebook.

CORRECTIONS FOR SAMPLES WITH HIGH WATER CONTENT

Concentrations of volatile compounds in soils must be reported on a dry weight basis, using the moisture content of the soil to adjust results. Routine procedures by the laboratories include this correction. Laboratories may not routinely correct results because of the effects due to the miscibility of the methanol with the water in the sample. The effects are to bias the results low, and if the moistures in the samples are high, these biases may be significant. The effects of this biases upon results should be considered when soils are sampled, and if necessary the laboratory instructed to correct results accordingly.

ELEVATED REPORTING LIMITS DUE TO HIGH MOISTURE

For samples with excess moisture, reporting limits may need to be elevated higher than levels routinely reported by the laboratory. Elevated reporting limits may be acceptable if they do not exceed applicable criteria. Historical site information and published information can be used to ascertain the range of moisture levels that can be expected. This can be used to determine if the biases are significant. Additional guidance regarding elevated reporting limits is available in RRD Operational Memorandum No. 2, Attachment 1.

OTHER METHANOL PRESERVATION PROCEDURES

Variations to the field procedure in this method may be used if approved in advance by the MDEQ. Important considerations are:

- Samples must be preserved in the field, a target ratio of 1:1 for the weight of the soil to the volume of methanol should be used.
- Samples must be sonicated for 20 minutes at the laboratory.
- A methanol aliquot must be taken and stored for analysis immediately after sonication that is sufficient for initial analysis, and analysis of any subsequent dilutions.
- Sufficient documentation to validate the data must be provided to the MDEQ.

FIELD SAMPLING PROCEDURE

1. Make arrangements with the laboratory to obtain appropriate Methanol Preservation Sampling Kits.
2. Record the tracking or lot number(s) for the methanol in the field notebook. If more than one lot is used, each lot must be associated with the samples for which it was used.
3. Prior to collection, check the calibration of the balance. See “Field Balance Calibration Check” on page 10 of this document.
4. Prior to collection prepare a temperature blank sample using tap water and a VOC vial.
5. Prior to collection prepare a sufficient quantity of methanol field blanks, i.e., at least one per cooler and one per methanol lot as follows:

   a) Select an area free of VOC sources.
   b) Remove a methanol tube from the wide mouth jar.
   c) Use scissors to cut off the top, and place the methanol into one of the pre-weighed sample vials.
   d) Place the cap on the vial and tighten it. Avoid over-tightening.
   e) Place a green sticker on the top of the cap.
   f) Record the identification of the vial as "Methanol Field Blank" on both the vial label and in the field notebook.

6. Calibrate the syringe to estimate the amount of soil needed to meet the target weight, and use that syringe as a comparison for how much sample is needed.

   Calibration is performed using steps 10 - 17 below, using the syringe only, and part of the soil that is to be collected. The soil used for calibration cannot be used as the sample. It must be extruded from the sampler and discarded at the site before collecting the sample. The sampler does not have to be cleaned between calibration using this step, and collection of the sample.

7. Place the wide mouth glass jar, used to prevent balance contamination, on the balance.
8. Record the location, date, and time of sampling in the field log book. Do not place any labels, stickers, tape, etc. on the pre-weighed sample vials.
9. For methanol field blanks, remove the cap from a methanol field blank which was prepared in Step 5 above, place the opened vial in the collection area for the approximate time it takes to collect a sample, and then cap the methanol field blank for storage and transport to the laboratory.
10. Place a pre-weighed VOC vial and syringe in the wide mouth jar on the balance.
11. Record the weight in the field log book. If the balance features re-zeroing, zero the balance.
12. Remove the syringe. If a cap is provided, remove the cap and place it in the jar.
13. Insert the open end of the syringe into a fresh face of undisturbed soil, and fill it as appropriate according to the calibration of the syringe (Step 6).
14. If necessary, use your gloved finger (decontaminate before next sample), or other appropriate instrument, and push the soil deeper into the syringe sampler.
15. If a cap was provided, immediately cap the end of the syringe.

16. Place the syringe in the jar on the balance. Read the weight, and if necessary, subtract the weight of the syringe, vial, and jar, as appropriate, to determine the weight of the soil.
17. If the weight of the sample is determined to be more than the maximum amount allowed, extrude enough soil to obtain the target amount within the specified tolerance, and re-weigh. See the table in this document, "Specifications for the Collection of Samples Using Methanol Preservation" for the applicable target sample size and tolerance.
18. If the weight of the sample is less than the minimum amount allowed, re-sample and repeat steps starting with Step 7.
19. Record the soil weight in the field notebook. DO NOT RECORD the weight on the sample vial label.
20. Remove the cap from the sample vial, and place it in the jar on the balance, with the septum upwards.
21. If the required amount of methanol is not included with the pre-weighed vial, immediately remove a methanol tube from the wide mouth glass storage jar, holding the tube upright use scissors to cut (plastic) off one end, and pour the methanol into the sample vial, taking care to avoid spillage.
22. Insert the open end of the syringe sampler into the mouth of the vial, and carefully extrude the soil, taking care to avoid spillage. Loss of several drops will not make a significant difference in the results. If a significant amount is spilled, a new sample must be collected, or the sample must be appropriately flagged to indicate estimated results.
23. Using a clean brush, paper towel, or other suitable material, thoroughly wipe excess soil particles from the threads and vial body. Particles left on the threads will prevent a good seal.
24. Place the VOC cap on the sample vial. The cap must be tight; however, over-tightening should be avoided.
25. Gently swirl the sample and methanol for about 10 seconds to break up the soil. DO NOT SHAKE.
26. Place the sample in a plastic bag on ice in a cooler.
27. Attach a green sticker on the plastic bag to indicate a hazardous waste.
28. Using the syringe sampler, take another sample from the soil.
29. Cap and label the syringe with the sample identification.
30. Place the syringe with the sample in the plastic bag. This sample is for dry weight determination.
31. Decontaminate the jar/balance using decontamination procedures appropriate for the type and level of contamination.
32. Unused methanol must be returned to the laboratory for disposal.